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Magnetic relaxation in nanoparticles of iron oxides : magnetic recording applications

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Abstract : The single domain anisotropic magnetic particles with high coercivity are suitable for magnetic recording and therefore magnetic relaxation effect which tends to destroy their magnetization is important. A quantum mechanical model was recently developed by the author to calculate the magnetic relaxation rate of nano-particles of iron oxides (magnetite and hemetite). These results have been applied to estimate their particle size for magnetic tapes/films on the consideration that the relaxation rate (magnetic fluctuation) must not be too high to wash out the magnetization produced by audio and visual electrical signals which operate at frequencies 10^2–10^6 and 10^9–10^{10} Hz respectively. In the first approximation it appears that particles of size 240–270 Å (diameter) are suitable for audio recording and those of 190–200 Å for video recordings. It is the first calculation of this type.

Keywords : Magnetic relaxation, recording, data storage, nano particles.

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1. Introduction

The magnetic nano-particles of iron oxides, especially magnetite (α-Fe_3O_4) and hemetite (Fe_3O_4), occur almost everywhere – in environment, minerals, geomagnetic deposits, animals, brain cells (human brain contains about 10^8 magnetic nano particles that might be responsible for various biological effects), plants, bacteria, *etc*. Their technological applications include ferrofluids, magneto-resistive devices, magnetic-sensors, magnetic recording and many more. The single domain particles exhibit unidirectional permanent magnetism (high coercivity but not too hard) which is exploited in these applications and therefore relaxation effects which tend to destroy magnetization are important. It is therefore desirable to examine the various facets of magnetic relaxation, both experimental and theoretical, for a better understanding of the phenomenon in view of their technological applications. Nanotechnology is likely to play a much greater role in future and hence nanophysics assumes a greater significance in general.

While the magnetic properties of small particles (or micromagnets) of different materials have been studied through several techniques (magnetization, hysterisis, ac susceptibility measurements, *etc*), the iron-bearing materials have been extensively probed through ^{57}Fe Mössbauer spectroscopy which provides a highly accurate method to study magnetic interactions and their dynamic effects at low temperatures [1,2]. Therefore, particular emphasis has been given to draw upon the Mössbauer studies of these compounds for testing the validity of the magnetic relaxation calculations. A brief discussion of the classical and quantum mechanical theories (along with experimental results) has been included for the sake of completeness, which is also essential to visualize the impact of the relaxation phenomenon on magnetic recording.

2. Nanoparticles for magnetic recording

Single domain anisotropic particles of α-Fe_2O_3 Fe_3O_4, CrO_2 *etc* were initially used for magnetic recording because of high coercive field of 200 to 500 Oe and these were usually produced by mechanical (ball milling) and thermal (annealing) treatments. Smaller particles are

desirable for greater data storage capacity per unit surface area of the magnetic tape. The quality of recording, frequency response, saturation magnetization, output signal strength *etc* depend on particle size, coercive force and the type of material (oxides or alloys). The α-Fe_2O_3 particles of length-breadth ratio 5 : 1 (length ≈ 5000 A°) has $H_c \approx 200$ Oe, while CrO_2 particles with length-thickness ratio 20:1 and $H_c \approx 500$ Oe worked as a better material for magnetic recording. Single domains can exist from 100 to 10,000 Å (10 to 1000 nm) with little change in coercivity (except for very small particles) and on a simple consideration the entire range of such particles may be considered useful for magnetic recording. Metallic alloys (Fe-Ni, Fe-Ni-Co, Cu-Fe-Ni) of smaller sizes and higher coercive fields were also used in the past years [3,4].

As the information (*i.e.* audio-visual data) has to be permanently stored, the magnetization must be stable and resistant to change. This requires that the materials have high magnetization, relatively high coercivity and a fairly rectangular hysterisis loop. At the same time, the coercive field must not be so high that the magnetization (or bit of information) cannot be switched on by a relatively small field of 2000–3000 Oe usually produced by the "write-head'. New materials with improved parameters have been developed over the years for high-density recording. Currently Co-based ternary alloys such as CoCrTa and CoCrPt are being used for the coating of magnetic tapes/films [5]. Their crystalline structure is mainly hexagonal close packed (hcp) with the uniaxial anisotropy along the *c* axis. The oxides and metallic alloys differ in their magnetic behavior and temperature dependent relaxation (fluctuation) because of various factors, including the fact that in oxides the super-exchange may be operative whereas in alloys the magnetic interaction is electron gas mediated.

It is natural to ask which materials, what sizes, what magnetic-thermal stability *etc* are ambient for such nano-particles? Is there any theoretical framework to throw light on these matters that can be exploited by the industry? Such questions have become relevant in recent years when greater data storage capacity in magnetic recording is required. The elements of magnetic relaxation theory can be fruitful in this respect. Temperature produces 'inherent' magnetic fluctuations (magnetic instability) which may be important in putting some boundary condition on the size of the particles for a given recording application. Possibly it is due to magnetic relaxation (fluctuation) that coercive force is reduced to zero (or a very small value) for particles of less than 50 Å leading to paramagnets [3].

The question arises – what short of magnetic fluctuations are tolerable up to room temperaiurcs (devices operate at room temperatures)? This should be related to the operating frequencies of audio-visual electrical signals. The former works within kHz to MHz (10^2–10^6) range while the latter works at GHz (10^9–10^{10}) level. A pheno-menological consideration indicates that particles for audio recording should be such that their magnetic relaxation rate lies within the range 10^2–10^6 sec^{-1} so that magnetization produced is not wiped out (because of thermal fluctuations) within the life-time of the electrical signals created by audio-pulses. Since audio frequency has a wide range, it may be desirable to use heterogeneous particles (of different sizes) with a broad range of relaxation rates. On similar considerations the magnetic recording of visual signals requires smaller particles (higher relaxation rates can be acceptable).

In order to calculate the absolute value of magnetic relaxation rate, it is important to have a reliable theory that gives the rate equation in terms of known and measurable properties of the given material. Unless this is done, it may not be possible to estimate the ambient particle size for magnetic recording applications. It is therefore necessary to have a microscopic theory of magnetic relaxation and its support through experimental results before the same can be adopted for magnetic recording applications.

It is obvious that the magnetic relaxation mechanism in oxides and metallic alloys could be different and the particles of the same size (in the two categories) may have much different relaxation rates at a given temperature. As a result these particles can show significantly different behavior for the purpose of magnetic recording or other application which exploits the finite magnetization of nanoparticles. The discussion that follows applies to iron oxides which are still important for different applications including bio-studies. This work is an off-shoot of the recent theoretical work [6] on the magnetic relaxation of iron-bearing superparamagnetic particles extensively studied through Mössbauer spectroscopy at low temperatures.

3. Magnetic relaxation mechanism

In Brown's model [7] for uniaxial particles the magnetization vector jumps between two directions (θ = 0, π) of the energy minima $E = -KV\cos^2\theta$ and relaxation rate is given by $R = R_0 \exp(-KV/k_BT)$ where K = anisotropy energy cm^{-3}, V = particle volume. The pre-exponential factor R_0 is a function of several variables like anisotropy energy, gyromagnetic ratio, magnetization, magnetic viscosity, temperature and random field which are often difficult to quantify, and therefore the net effect is conveniently replaced by this parameter (or attempt frequency). For ultra-fine particles of α-Fe_2O_3 (magnetite) and Fe_3O_4 (hemetite) $R_0 \approx 10^{10}$–10^{12} sec^{-1} as determined from Mössbauer magnetic spectra at low temperatures. However, its value at room temperature could not be extrapolated without a reliable theory.

A quantum mechanical model has been developed to calculate magnetic relaxation rates for uniaxial nano-particles (or superparamagnets) as a function of temperature and particle size (diameter). The relaxation proceeds with an exchange of energy between magnons and phonons *via* two-magnon one-phonon scattering, and the final results are summarized as [6] :

$$R = R_0(T)\exp(-KV/k_BT), \tag{1}$$

where,

$$R_0(T) = (9\hbar/64M\pi^2)(2J'S)^2(T_D^2/T_C^7)$$
$$\times(T^3/k_B^2)\exp(-T_D^2/4T_CT)$$
$$\times\left[8.85(\theta_C/T)^{3/2} + (5/12\pi^4)(\theta_D/T^3)\right]. \tag{2}$$

Here, M = mass of Fe atom, S = spin of Fe, $J' = dJ/dR_{mn}$ = dynamic exchange, $T_D = \theta_D/4$, θ_D = Debye temperature, $T_C = \theta_C/7$, θ_C = Curie temperature. For magnetite and hemetite $\theta_D \approx 700$ K, $\theta_C = 950$ K, $K = 10^5$ erg cm^{-3}, exchange integral $J_0 = 2 \times 10^{-3}$ eV (or 21 K) and $J' = 2.12 \times 10^{-6}$ erg cm^{-1}. Also $V = Na^3$ where N = number of Fe atoms and $a \approx 5$ Å (lattice dimension).

The above expressions are obtained considering the situation that in small particles the uniaxial magnetization vector fluctuates between the two possible directions (parallel and anti-parallel) due to flow of thermal energy to the magnetic slates, and in the quantum mechanical description it constitutes a coupling between 'spin waves' and 'lattice vibrations' (or magnons and phonons). Effectively it is the dynamic exchange interaction that decides the degree of coupling and therefore both the magnetic and lattice parameters come into play. The detailed description [6] shows that during a two-magnon one-phonon scattering process (of lowest order) the number of magnons remains unchanged but the number of phonons changes and the flow of energy (between magnons and phonons) per second is proportional to the rate of change of phonon number.

4. Experimental support

The validity of these relations can be tested through comparisons between theoretical and measured values of R_0 and R by an experimental technique (a given method can detect relaxation rate within a certain range only). Calculations show that $R_0 = 1.1 \times 10^9$ to 6.6×10^{12} for T = 10 to 100 K which covers the values (10^{10}–10^{12} sec^{-1}) often used in the fitting of Mössbauer magnetic spectra of fine particles at low temperatures [8,9]. This agreement is quite remarkable.

Magnetic measurements at low temperatures through different techniques made to test the validity of Brown's model (expression I) have remained inconclusive because of uncertainly about the size of the particles. Barra *et al* [10] studied the superparamagnetic relaxation of 8Fe molecular cluster system by ESR, alternating susceptibility and Mössbauer spectroscopy (first such combination of methods) at low temperatures and obtained R_0 (T) = 5.3 $\times 10^6$ sec^{-1}. The expression (2) gives R_0 (T) = 1.4 $\times 10^6$ sec^{-1} at 5 K and 1.1 $\times 10^9$ sec^{-1} at 10 K, which shows that the agreement with the experimental data is quite good. Though the value of R_0 depends on the material, it should remain comparable within an order of magnitude for iron group systems. For the first time Wemsdorfer *et al* [11] conducted the magnetization measurement of single nanoparticles of at low temperatures, obtained hysterisis curves for fcc Co particles of mean diameter 25 ± 5 nm (250 ± 50 Å) and found that R_0 (T) ~ 2,5 $\times 10^8$ sec^{-1}. It is similar to iron-based magnetic particles in a qualitative manner.

5. Application to magnetic recording

Once the theoretical framework is accepted with a reasonable degree of confidence its projections can be applied to magnetic recording. This is what has been presented in this section. The magnetic relaxation rates at room temperature for iron oxide particles of different

sizes have been calculated and given in Table 1. Calculations for smaller particles may be seen elsewhere [6].

Table 1. Magnetic relaxation rate for nano-size particles of iron oxides at 300K.

$T(K)$	$R_0(sec^{-1})$	Size(Å)	$R(sec^{-1})$
300	5.05×10^{11}	134	2.47×10^{12}
		169	1.20×10^{11}
		192	5.91×10^{9}
		229	1.42×10^{7}
		236	3.12×10^{6}
		243	6.90×10^{5}
		256	3.37×10^{4}
		267	1.65×10^{3}
		277	7.98×10^{1}
		287	3.94×10^{0}

The relaxation rate changes rapidly with particlesize and it affects the magnetic behavior very sharply. The particles of 240–270 Å could be efficient for the magnetic recording of audio signals and those of about 190 Å for visual signals. In a way it puts a limit on the size of the particles of iron oxides for magnetic recording, that is, particle smaller than 240 Å may not be efficient for sound recording and similarly particles smaller than 190 Å may not be efficient for video recording. This puts an upper limit on the areal density of recording tapes using iron oxides or other compounds of iron-group transition elements.

It has already been said that the physics of CoCrTa or CoCrPt alloys (currently being used) may be different from those of iron oxides yielding significantly different results. A proper theoretical study will be taken up in due course. However, one may get an inkling of the results on the following considerations. Alloying creates 'single domains' of magnetic materials and gives higher coercivity necessary for magnetic recording. Also, the anisotropy energy in metallic alloys is usually higher. For example $K \approx 3 \times 10^5$ ergs cm^{-3} in copper-iron-nickel alloys. It could be still higher for cobalt based alloys because cobalt has *hcp* structure with $K \approx 10^6$ ergs cm^{-3}. Their particle size for magnetic recording could be appreciably smaller making them suitable for greater areal density of tapes/films. This is in line with the current position.

6. Conclusions

The magnetic relaxation theory for nanoparticles has been applied to examine their magnetic recording applications for audio-visual signals. The ambient size of iron oxide particles for such applications has been derived from a theoretical consideration and it appears to be the first attempt of this type. The results derived can be applied to other devices and sensors that utilize magnetic nanoparticles.

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